Use of palm oil decanter cake as a new substrate for the production of bio-oil by vacuum pyrolysis

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ABSTRACT

The present study was carried out to investigate the potential of palm oil decanter cake (PDC) for bio-oil production at various temperatures by vacuum pyrolysis. PDC was first dried in oven at 105 °C for 24 h to remove moisture and ground to particle size of 0.85–2 mm. Pyrolysis experiments were carried out at 400, 450, 500, 550 and 600 °C, with heating rate of 15 °C/min. The highest yield of bio-oil (22.12 wt%) was obtained at pyrolysis temperature of 500 °C. The chemical characterization of bio-oil was studied using ^{1}H NMR, FTIR, CHNS analyzer and GC–MS. The other properties like pH, calorific value and thermal volatilization were also determined. The pH value recorded to be 6.38, which is found to be higher as compared to other bio-oils. The calorific value of PDC bio-oil found to be 36.79 MJ/kg, which is slightly lower than that of conventional liquid fuel such as gasoline and diesel fuel. However, the bio-oil obtained from PDC has better fuel characteristics than that of bio-oil derived from palm kernel shell (PKS).

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1. Introduction

World's energy consumption is increasing significantly in recent decade due to economic and population growth. International Energy Agency forecasts that global energy demand will increase by one third from 2007 to 2035. However, the share of fossil fuel in world's energy mix will decrease from 82% to 76% in 2035 while renewables share in primary energy use rises to 18% in 2035, from 13% in 2011 [1]. In addition, depletion of fossil fuel resources and uncertainty of oil price encourage the search for biomass based renewable energy sources due to their local availability, affordability and sustainability. Employing biomass as energy source is likely to be an attractive option for reducing greenhouse gas emission due to its ability to deliver a significant reduction in net carbon emission when compared with fossil fuels [2–4]. Combustion of biomass is considered to be CO_2 neutral as it can be captured from atmosphere by photosynthesis process [5,6].

Oil palm industries can be considered as potential resources for generation of renewable energy. From the processing of fresh fruit bunch (FFB), palm oil milling plant produces 23.5 wt% as crude palm oil (CPO), 5.2 wt% as crude palm kernel oil (CPKO) while the rest, 71.3 wt%, is released into the environment in the form of solid or aqueous phase [7]. Decanter cake (PDC) is generated by palm oil milling plant from three-phase CPO purification. The production rate of PDC is about 4–5 wt% of fresh fruit bunch processed. This is equivalent to around 3.6 million tonnes of PDC generated by Malaysian palm oil industries in 2012. At the oil palm mill site, the PDC generated take up a lot of space. Moreover when dried, the PDC become fire hazard and contribute toward increasing the amount of suspended particles in the vicinities of mills. Recently, PDC has been utilized as feedstock for the production of cellulose and polyose [8,9], bio-surfactant [10], bio-butanol [11], and bio-diesel [12]. So far, there is no report on thermal conversion of PDC into bio-oil through pyrolysis process.

Biomass is converted into energy sources through thermal, biological, mechanical or physical processes [13]. Biomass is heated in the absence of oxygen to 275–675 °C during thermal conversion via pyrolysis to produce portion of gas, liquid (condensable gases) and carbon rich solids [14]. The relative amount of each fraction depends on the initial feedstock type and mode of pyrolysis. Fast pyrolysis (residence time less than 2 s) at 400–600 °C produces up to 75% liquid fraction, while slow pyrolysis generates lesser liquid fraction and more solid fraction. A specific process, gasification, converts almost 90% of biomass into gas fraction [15]. Pyrolysis for liquids production is currently of particular interest as the liquid can be stored and transported, and used for chemicals synthesis or as an energy carrier [13].

Vacuum pyrolysis is usually conducted in slow or intermediate rate pyrolysis mode. Vacuum pump is employed to evacuate the air

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before heat treatment of biomass and withdraw the vapor during thermal decomposition of biomass. Typically, yield of liquids by vacuum pyrolysis is about 20–40 wt%, which is comparable with that of slow pyrolysis [16]. Simple reactor design and no requirement of inert gas made up the advantage of vacuum pyrolysis compared to fast pyrolysis mode. Liquid product of pyrolysis is usually divided into two phases: aqueous phase and non-aqueous phase. The aqueous phase pyrolysis liquid contains lower molecular weight oxygenated organic compound, while organic compounds particularly aromatics becomes main constituent of non-aqueous phase [17]. Bio-oil obtained by pyrolysis process typically contains 55–65 wt% C, 5–7 wt% H, 28–40 wt% O and small amount of N and S (less than 0.5 wt%) [18].

Generally, bio-oil compounds can be classified into acids, esters, linear aldehydes and ketones, cyclic ketones, furans, alcohols and sugars, ethers, phenols, phenolic ethers, oxygenated cyclic compounds, hydrocarbons and derivatives, and nitrogen compounds [19,20]. However, several factors e.g. feedstock type, pyrolysis condition, condensation procedures determines the chemical compositions of bio-oils [21]. High oxygen content of bio-oil is a major concern since it causes the instability of bio-oil, low calorific value and high acidity [22]. It can be resolved by upgrading through hydro-treatment process over heterogeneous catalysts [23,24].

Lignocellulosic biomass wastes are commonly used as substrate in bio-oil production via pyrolysis. In addition edible/non-edible oil cakes were also considered as potential raw materials for bio-oil production. The pyrolysis of soybean oil cake [25], rapeseed oil cake [26,27], sunflower [28], palm kernel cake [29,30], and sesame cake [31] has already been reported. The oil content of PDC was reported to be about 11.5 wt% [12]; therefore, it has the potential to be utilized as bio-oil substrate. A commercially viable process for converting PDC into bio-oil would facilitate removal of PDC, ensure formation of useful valuable by product and make the oil palm industry eco-friendly. Therefore, the present study was aimed to convert PDC into bio-oil through vacuum pyrolysis. The study also discusses the effect of pyrolysis condition on product distribution, and properties of PDC bio-oil in comparison with PKS bio-oil.

2. Materials and methods

2.1. Materials

PDC and PKS were collected from LKPP Sdn. Bhd. palm oil milling plant in Lepar Hilir, Kuantan, Pahang, Malaysia. The samples were dried in oven at 105 °C for 24 h to remove moisture. Dried decanter cake was then ground and sieved to obtain the particle size of 0.85–2 mm.

2.2. Vacuum pyrolysis

The pyrolysis of biomass was carried out in a cylindrical stainless steel reactor with inner diameter of 6.5 cm and height of 12 cm. The pyrolysis apparatus is illustrated in Fig. 1. About 300 g of biomass was loaded into the reactor that was then sealed and positioned into a muffle furnace. A vacuum pump was used to evacuate the air inside the reactor and kept the pressure below 30 kPa. The reactor was heated at 15 °C/min to the desired reaction temperature of 400, 450, 500, 550 and 600 °C. Vapor evacuated from the pyrolysis process was condensed using water condenser and water-ice condenser traps. Uncondensed gases were discharged into air properly. The pyrolysis processes was terminated after an hour at the final temperature or when liquid was not produced anymore. Liquid product separated into two phases: organic and aqueous phase. The organic phase obtained i.e. the bio-oil, is

labelled as PDC-400, PDC-450, PDC-500, PDC-550, and PDC-600, with the pyrolysis temperature serving as part of the label. For comparison purposes, dried PKS was also pyrolyzed at 500 °C. The bio-oil produced was labelled as PKS-500. All of the bio-oil samples were analyzed to determine their properties and chemical compositions.

2.3. Characterization of bio-oil

2.3.1. Higher heating value

Calorific value of bio-oils was measured using IKA C-200 oxygen bomb calorimeter. Approximately 0.2 g of bio-oil was placed into a quartz crucible inside the combustion chamber. Pure oxygen gas was introduced into the chamber until 30 bar pressure was achieved. Two litres of tap water at temperature range of 20–23 °C was added inside the calorimeter surrounding the chamber. After five minutes of stirring, the water temperature became stable and the samples were ignited. The changes in water temperature were monitored until it remained constant. Differences of initial and final temperature were used to calculate the heating value of the samples. The calorimeter heat capacity was calibrated using benzoic acid as reference.

2.3.2. pH

Mettler Toledo SevenEasy pH meter was used to determine the pH of bio-oil. Each measurement was done in triplicate to give the average of the measurements.

2.3.3. Viscosity and density

Dynamic viscosity of bio-oils was determined by Brookfields DV-II+ viscometer equipped with Small Sample Adapter. Density of bio-oil was measured using KEM Densitometer. Viscosity and density of Automotive Diesel Oil (Caltex) were also measured for comparison purpose.

2.3.4. Elemental analysis

The composition of C, H, and N elements in bio-oil were determined by Elementar CHONS Analyzer. Oxygen content of bio-oil was calculated by differences.

2.3.5. Fourier transform infrared spectrometry

FTIR spectra of the bio-oils were obtained by Perkin Elmer Spectrometer. A thin film of bio-oil was placed between KBr plates and 100 scans of spectrum in 400–4000 cm^{-1} range were accumulated. A blank KBr plate was used as background of the measurement.

2.3.6. ^{1}H nuclear magnetic resonance

The nature of hydrogen in the bio-oil and the aliphatic, olefinic and aromatic components in bio oils were examined by Bruker NMR. Bio-oil sample was diluted into deuterated chloroform as solvent prior to analysis.

2.3.7. Gas chromatography–mass spectrometry

Analysis of bio-oil composition was performed on HP 6895 GC–MS equipped with Agilent 5973 mass selective detector. A HP DB-Wax capillary column (30 m × 0.25 mm × 0.25 μm) was employed to separate the constituents. Bio-oil was diluted in hexane then 1 μL sample was injected into column at 250 °C. Helium was used as carrier gas at flow rate of 1 mL/min. Oven temperature was programmed from 40 to 250 °C with heat ramp 8 °C/min, held at initial and final temperature for 10 min.

2.3.8. Thermogravimetry analysis

Thermal volatilization of bio-oil was evaluated by Mettler Toledo TGA/DSC unit. Experiments were performed involving 5 mg sample, 50 mL/min nitrogen flow with 10 °C/min heating
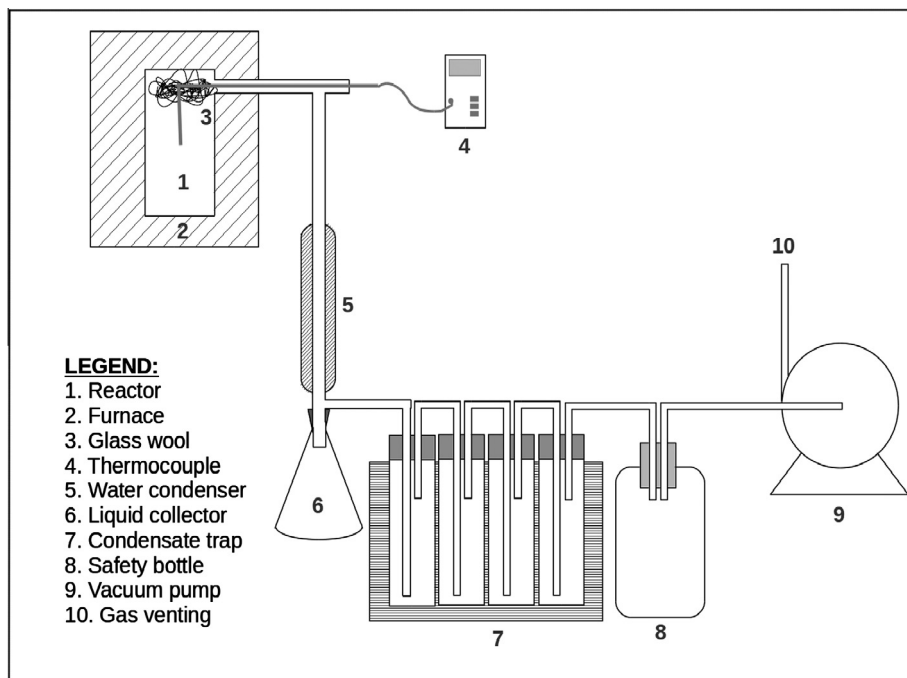
Fig. 1. Equipment layout for vacuum pyrolysis.

rate. The TG and DTG curves for bio-oils were recorded from 25 to 1100 °C.

3. Results and discussion

3.1. Bio-oil yield

During the pyrolysis process, biomass decomposed into gas, liquid and solid products. The composition of each product is influenced by the pyrolysis condition. The effect of temperature on PDC bio-oil yield is shown in Fig 2. Yield of products was determined by calculating the ratio of product weight over biomass feed weight. Char yield decreased as temperature increases, i.e. from 48.07 wt% at 400 °C to 38.57 wt% at 500 °C. However, char yield remained constant at temperature 500–600 °C. At higher pyrolysis temperature, more uncondensed gas was produced. In this study, gas yield increased from 17.41 wt% to 25.74 wt% at temperature of 400 and 600 °C, respectively. Total liquid produced by PDC pyrolysis was 34.52 wt% at pyrolysis temperature of 400 °C and increased to 39.66 wt% and 41.31 wt% for pyrolysis temperature of 450 and 500 °C respectively. Bio-oil was obtained by physical separation of total liquid product into organic and aqueous phase. Organic phase yield, referred as bio-oil, proportionally follow the trend of total liquid yield, increased from 18.72 wt% to 22.12 wt% at 400 °C and 500 °C, respectively. Maximum liquid yield was achieved between 500 and 550 °C; then started to decrease at higher pyrolysis temperature. This result is similar to that of other researches that indicated maximum bio-oil yield was obtained at around 500 °C. For example, Abdullah and Gerhauser [32] reported pyrolysis of oil palm EFB (empty fruit bunch) in fluidized bed reactor reached the maximum liquid yield at 500 °C, while soybean cake [25] and rapeseed cake [27] pyrolysis produced maximum yield of bio-oil at 550 °C. In the initial stage of pyrolysis process, aqueous pyrolysis liquid was formed due to dehydration at below 300 °C. Yield of bio-oil increased at temperature of 450–550 °C as primary tars from biomass solids started to form. At higher temperature, the yield of bio-oil started to decrease due to the secondary conversion of the primary volatiles [33].

3.2. Bio-oil properties

As shown in Fig. 3, the pH and HHV of PDC bio-oil initially increased with temperature, and then remained relatively constant at temperature range of 500–600 °C. It is reported that hemicellulose and cellulose first decompose at lower pyrolysis temperature. Meanwhile, lignin is the biomass component of the highest thermal resistance that decompose at 400–700 °C [33]. Low pH and calorific value of bio-oil produced at low pyrolysis temperature might be due to the decomposition of hemicellulose and cellulose.

The bio-oil derived from PDC has different characteristic compared to that of bio-oil derived from cellulosic materials, particularly its pH, calorific value and chemical composition. In this study, bio-oil derived from PKS was used as comparison. At 500 °C, PDC produced 22.12 wt% bio-oil, while PKS pyrolysis produced slightly lower yield of 18.76 wt% as illustrated in Fig. 4. The total liquid yield for both substrates was around 42%. This yield is lower than that of fast pyrolysis (typical yield ~75%) and
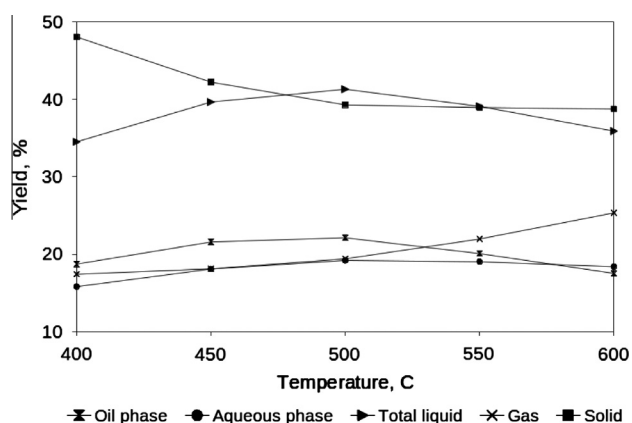

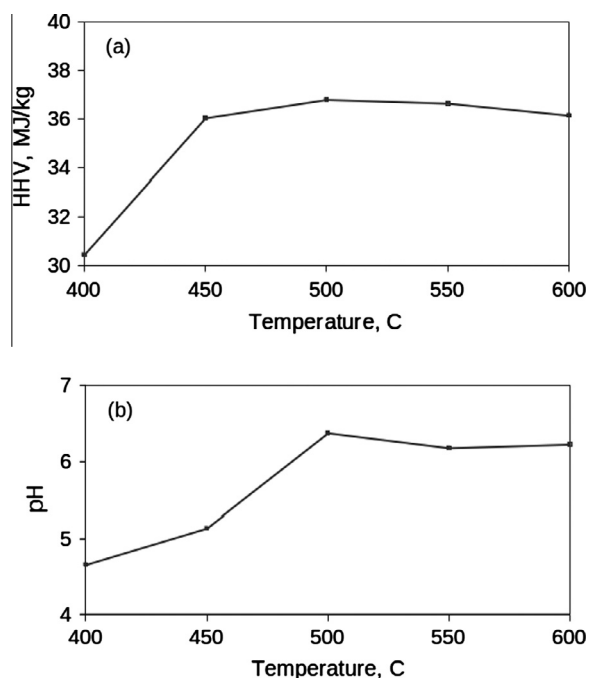**Fig. 2.** Effect of pyrolysis temperature on product yields from PDC.

Fig. 3. Effect of pyrolysis temperature on HHV (a) and pH (b) of bio-oil from PDC.
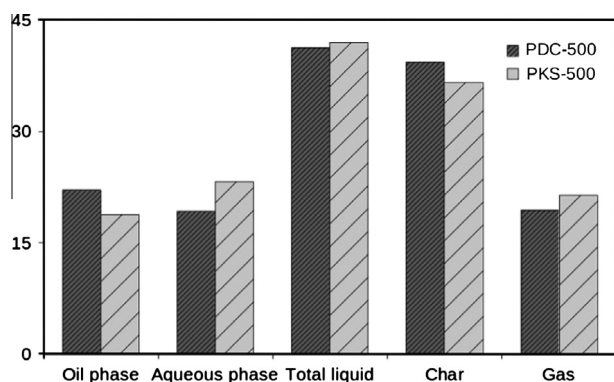

Fig. 4. Product yield comparison between PDC-500 and PKS-500.

quite similar with that of intermediate pyrolysis (typical yield ~50% in two phases) [13]. This results is also in agreement with previous works which reported about 40–60% of liquid obtained

from vacuum pyrolysis of biomass [16,34–36]. Table 1 provides pH and calorific value of PDC-500, PKS-500 and other bio-oil from various biomasses. Typically, bio-oil from cellulosic biomass including PKS has low pH as well as low calorific value. The calorific value and pH of bio-oil derived from decanter cake was higher than that of other bio-oil. This could be due to the high oil content in PDC, as was also observed for bio-oil produced from soybean oil cake (33.6 MJ/kg) [37]. This value is comparable to the calorific value of petroleum fuels, which are 47.3, 45.7 and 42.9 MJ/kg for gasoline, diesel oil and heavy fuel oil, respectively [38].

At 25 °C, the density of PDC-500 and PKS-500 are 1.0496 and 1.0499 g/cm^3, respectively; higher than that of diesel oil (0.8368 g/cm^3). The viscosities of PDC-500 and PKS-500 at 25 °C are 96.3 and 28.1 cP, respectively, that are also higher than that of diesel oil (4.42 cP). According to Mortensen et al. [18], typical viscosity and density of bio-oil is within the range 40–100 cP and 1.05–1.25 g/cm^3, respectively. However, Nolte and Liberatore [39] reported some type of bio-oils had lower viscosity than that range, particularly bio-oil derived from hardwood (15 cP), oak (6 cP), pine (26 cP), softwood (10 cP), and wheat straw (20 cP). Viscosity is influenced by water content of bio-oils and generally oil with higher water content has lower viscosity [39,40]. High viscosity of fuel caused problems in internal combustion due to poor atomization, incomplete combustion, and carbon deposition on the injection nozzles and inside combustion chamber [41]. Blending with the conventional fuel can resolve the high viscosity problem of bio-oil as well as through catalytic upgrading process.

3.3. Elemental analysis

The elemental analysis result indicates that the produced bio-oil consisted mainly of carbon and oxygen. The empirical chemical composition of PDC-500 and PKS-500 is $CH_{1.85}O_{0.19}N_{0.04}$ and $CH_{2.53}O_{0.76}N_{0.01}$, respectively. PDC-500 has lower O/C ratio than that of PKS-500. High O/C ratio is associated with lower calorific value and instability of bio-oil. Therefore, upgrading process of the bio-oil such as through catalytic hydrotreatment is required prior to its direct use as fuel for internal combustion engine.

3.4. FTIR analysis

FTIR spectra of bio-oil are shown in Fig. 5. The presence of water impurities and other polymeric O—H in the oil were indicated by the broad absorbance peak of O—H between 3600 and 3300 cm^{-1}. The presence of alkyl and aromatic groups was indicated by the strong absorbance peak of C—H vibrations at 2922 and 2852 cm^{-1}. Peak at 1707 cm^{-1} represent C=O stretch indicating the presence of

Table 1
Yield and properties of bio-oil.

| Biomass	Yield (wt%)	Elemental composition (wt%)						pH	HHV, MJ (kg^{-1})	Ref.
		C	H	N	O[a]	H/C	O/C			
PDC-500	22.12	68.91	10.65	3.00	17.44	1.85	0.19	6.38	36.79	This study
PKS-500	18.76	44.60	9.42	0.84	45.14	2.53	0.76	2.29	19.54	This study
PKS	48.70	47.60	8.10	0.60	43.70	2.05	0.69	3.27	17.90	[42]
Palm kernel cake	42.84	78.20	8.90	3.56	8.96	1.38	0.09	–	27.74	[29]
Palm trunks	25.00	45.21	6.54	1.78	46.45	1.74	0.77	3.00	28.04	[43]
Palm EFB	55.14	69.35	9.61	0.74	20.02	1.66	0.22	–	36.06	[44]
Soybean oil cake	25.81	67.89	7.77	10.84	13.50	1.37	0.15	–	33.60	[37]
Cottonseed cake	41.00	73.31	10.09	4.73	11.87	1.65	0.12	–	20.81	[45]
Rapeseed cake	58.20	70.20	10.00	5.10	14.10	1.71	0.15	6.9	32.80	[27]
Sesame cake	58.50	55.80	8.34	7.00	28.91	1.80	0.39	–	25.50	[31]
Mustard cake	53.20	58.46	8.52	5.86	26.67	1.74	0.34	–	25.10	[31]
Neem cake	32.10	73.81	8.79	1.88	15.59	1.43	0.15	–	30.00	[31]
Sunflower cake	48.69	59.81	6.22	4.87	29.10	1.25	0.36	–	15.86	[46]

[a] By difference.
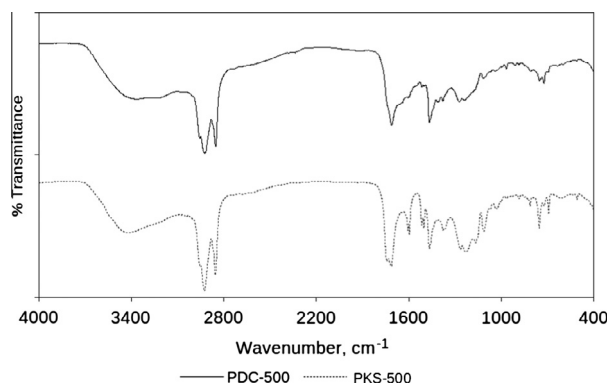
Fig. 5. FTIR spectra of bio-oils.

ketones and carboxylic acids. The presence of aromatics was indicated by absorbance peaks at 1460 and 721 cm^{-1}. According to the FTIR spectra, PKS-500 contains more oxygenated and aromatic compounds compared to that of PDC-500 as indicated by peaks at 1714, 1606, 813, 753 and 692 cm^{-1}.

3.5. ^{1}H NMR spectra

Fig. 6 clearly shows that the ^{1}H NMR spectra of bio-oil can be divided into three main regions: aromatic, olefinic, and aliphatic, based on the chemical shifts of specific proton types. Aromatic, olefinic, and aliphatic resonances occur in the chemical shift regions of 9.0–6.0, 6.0–4.0, and 3.0–0.5 ppm, respectively. ^{1}H NMR result indicates PKS-500 contains more aromatic component, while PDC-500 is dominated by aliphatic protons.

3.6. Gas chromatography–mass spectrometry

GC–MS was also employed to identify the chemical compounds present in bio-oil. Fig. 7 shows the chromatograph of bio-oil, while Table 2 provides the major chemical constituent of bio-oils. The most prominent differences of chemical constituent between PDC-500 and PKS-500 were the presence of phenolic compound in PKS-500. Quantitatively, more than 45% of PKS-500 was phenolic compounds that included phenol (9.70%), guaiacol (5.68%), isocreosol (5.01%), 4-ethylguaiacol (5.86%) and syringol (5.57%). Phenolic compounds were derived from cellulosic materials of
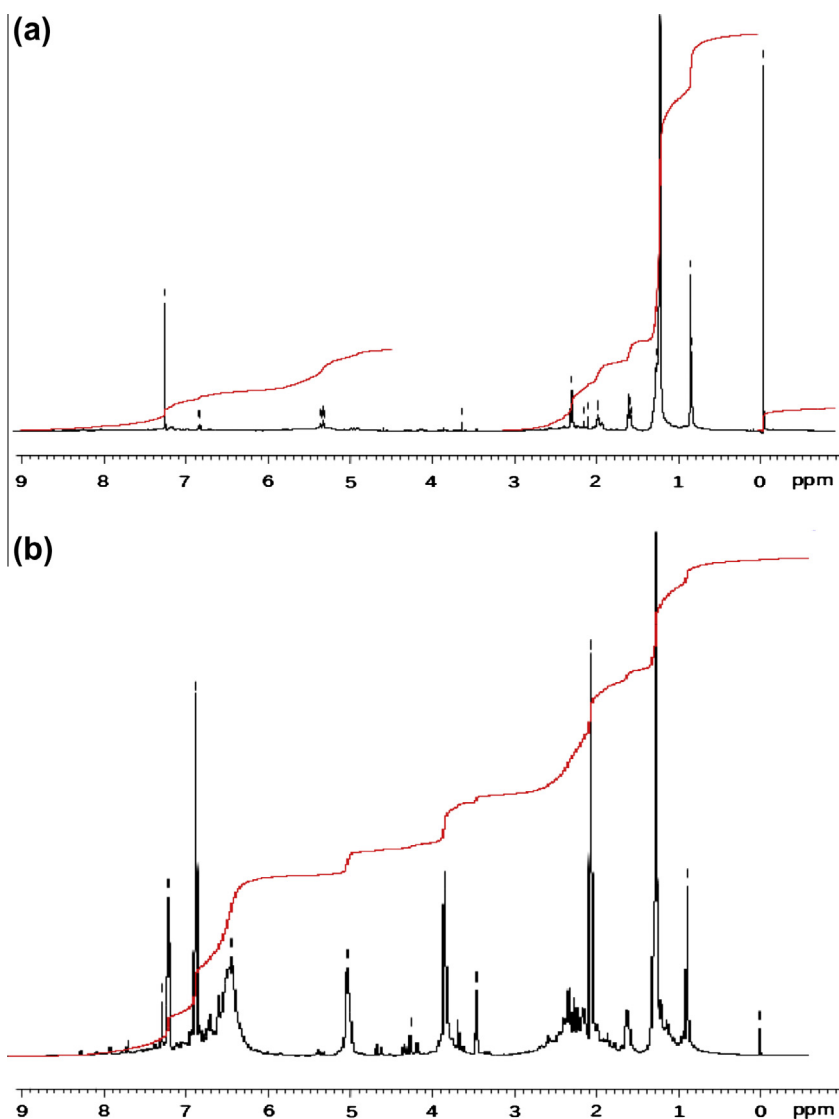

Fig. 6. ^{1}H NMR spectra of (a) PDC-500 and (b) PKS-500.

PKS. PDC-500 contained a small amount of phenol (about 3%) compared to that of PKS-500. Major component of PDC-500 was aliphatic hydrocarbon and aliphatic carboxylic acid with number of C atom between 16 and 18.
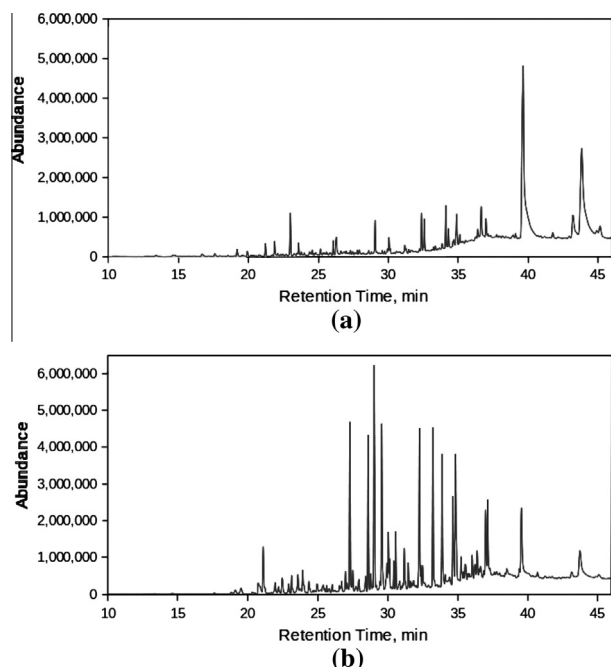
3.7. Thermogravimetry analysis

Thermal analysis of bio-oil using TGA/DTG shows that PKS-500 tends to volatilized at lower temperature than PDC-500 as shown in Fig. 8. It is also noted that the boiling range of phenolic compounds (180–260 °C) is lower than that of aliphatic hydrocarbon or carboxylic acid with C number 16–18 (270–350 °C). This is consistent with GC–MS, FTIR and NMR analysis, which indicate that the major constituent of PKS-500 was aromatic compounds, while that of PDC-500 was aliphatic. The presence of very small residual mass of less than 0.5%, in PDC-500 at temperature above 600 °C indicated that the bio-oils almost totally degraded or vaporized during the thermal treatment. PKS-500 tends to be polymerized
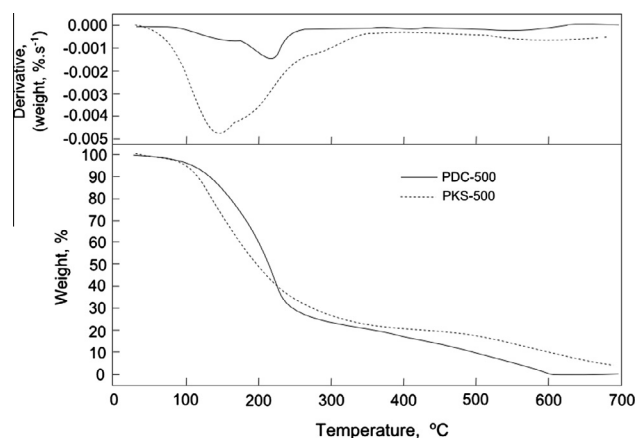

Fig. 7. Chromatogram of (a) PDC-500 and (b) PKS-500.

Fig. 8. DTG and TGA plots of bio-oil.

Table 2
Major chemical constituent of bio-oil determined using GC–MS.

Peak No.	Retention time (min)	Chemical compound	Peak area (%)	
			PDC-500	PKS-500
1	20.761	Butyric acid	–	1.2278
2	21.122	Furfural	–	2.0163
3	22.987	Pentadecane	2.4843	–
4	26.283	8-Heptadecene	1.7487	–
5	27.313	2-Methoxy phenol	–	5.6790
6	28.617	2-Methoxy-5-methylphenol	–	5.0119
7	29.041	Phenol	1.2446	9.7042
8	29.584	4-Ethyl-2-methoxy-phenol	–	5.8653
9	29.962	2-Ethyl-phenol	–	1.3728
10	30.054	4-Methyl-phenol	–	1.9234
11	30.580	2-Methoxy-4-propyl-phenol	–	1.7024
12	31.198	4-Ethylphenyl acetate	–	1.5004
13	32.279	2,6-Dimethoxy-phenol	–	5.5680
14	32.377	14-Methyl-pentadecanoic acid, methyl ester	2.7031	–
15	32.577	2-Heptadecanone	1.2936	–
16	33.241	1,2,3-Trimethoxybenzene	–	5.4974
17	33.893	Hydroquinone mono-trimethylsilyl ether	–	4.4567
18	34.122	Pentadecanenitrile	2.9015	–
19	34.665	4-Propyl-1,1′-diphenyl	–	3.4006
20	34.849	Dodecanoic acid	–	6.4705
21	34.889	9-Octadecenoic acid, methyl ester	3.2523	–
22	35.249	2,6-Dimethoxy-4-(2-propenyl)-phenol	–	1.1162
23	36.044	N-(4-Methoxyphenil)-2-hydroxyimino acetamide	–	1.0707
24	36.405	Homovanillyl alcohol	–	1.2525
25	36.651	Oleanitrile	2.8186	–
26	37.000	Tetradecanoic acid	–	2.5028
27	37.149	2,6-Dimethoxy-4-(2-propenyl)-phenol	–	2.9996
28	39.546	N-Hexadecanoic acid	34.3531	3.6247
29	43.214	Octadecanoic acid	4.7770	–
30	43.769	6-Octadecenoic acid	28.8344	2.8586
31	44.925	3-[(2-Methoxyethoxy)methoxy]-2-methyl-tricycloundecanone	1.4889	–
32	45.154	Hexadecanamide	1.8873	–

at high temperature as indicated by higher percentage (3%) of residual mass in PKS-500 at the end of thermal treatment.

4. Conclusion

In this study, decanter cake from palm oil milling plant was pyrolyzed under vacuum conditions to investigate the effects of temperature on product characteristics. Palm oil kernel shell was also pyrolyzed for comparison purposes. The maximum oil yield of 22.12% was obtained at a final pyrolysis temperature of 500 °C. The PDC-500 bio-oil is a mixture of aliphatic and aromatic compounds having an empirical formula of $CH_{1.85}O_{0.19}N_{0.04}$ and an H/C atomic ratio of 1.85 at optimum conditions. GC–MS analysis indicates that the PDC-500 composition was dominated by aliphatic hydrocarbons and carboxylic acid molecules containing 16–18 carbons, while PKS-500 contained phenolic compounds as major constituent. NMR analysis of bio-oils indicated that PKS-500 has higher aromatic content than that of PDC-500. The higher calorific value of PDC-500 is 36.79 MJ/kg, which is comparable to those of petroleum fuels calorific value. The main advantages of bio-oil derived from decanter cake are higher pH value and no tendency to be polymerized at higher temperature. However, high oxygen content of bio-oil causes low calorific value and low oil stability. It means that upgrading process e.g. catalytic cracking or hydrodeoxygenation of bio-oil is required prior to being used directly or as an additive to the conventional fuels.

Acknowledgements

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